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Plasmonic dispersion engineering of coupled metal nanoparticle-film systems

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The plasmonic dispersion properties of thin silver films in close proximity of square-periodic arrays of silver nanocylinders are investigated via transmission measurements and numerical simulations. Due to their nanoscale thicknesses, these films support hybrid surface plasmon modes extended across both interfaces, whose dispersion curves exhibit a large geometrically tunable energy splitting. Furthermore, the spatial and spectral overlap between these modes and the nanoparticles' localized plasmonic resonances produces an additional anticrossing in the dispersion spectrum. The resulting plasmonic excitations are attractive for applications given their wide tunability, coupling to free-space radiation, and ability to extend into an optically active substrate.

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I. INTRODUCTION

The phenomena of surface plasmon polaritons (SPPs) and localized surface plasmons (LSPs) have been the subject of extensive research in recent years,¹ due to the unique advantages that they provide over dielectric-based photonic excitations. SPPs are propagating surface charge oscillations at the interface between a metal and a dielectric that result in a deep sub-wavelength confinement of the electromagnetic fields near the interface. In practice, momentum matching components such as prisms or gratings are required to couple these modes with free-space radiation. LSPs are resonant oscillations of the electron gas in metal nanoparticles (NPs) that result in highly localized electromagnetic fields in the NPs near-field zone. The LSP resonance is dependent upon the NP size, shape, and composition and on the permittivity of the surrounding dielectric medium. SPPs and LSPs have been employed in many applications that leverage the properties of sub-wavelength confinement accompanied by spectral tunability, including Raman spectroscopy, light emission efficiency enhancement, and ultra-compact optical waveguides.¹

Recently, the interaction between the LSPs of a two-dimensional NP array and the SPPs supported by a nearby metal-dielectric interface has been studied,^{2–6} as the combination of these two basic excitations can provide additional degrees of freedom for fundamental studies and applications. In this configuration, the NP array provides additional in-plane momentum to incident light that allows it to couple with the SPP modes, as required, e.g., for light injection into and extraction from plasmonic waveguides.³ Additionally, the spatial and spectral overlap between LSPs and SPPs can produce an anticrossing in the plasmonic dispersion curves and geometrically tunable mixed resonances, which have been exploited recently for the demonstration of doubly resonant Raman spectroscopy.⁶ These previous reports have

focused on the coupling between LSPs and a single branch of SPP modes supported by a single metal-dielectric interface. In the present work, we consider instead the use of very thin metal films embedded in a symmetric dielectric environment (and again positioned in the near-field of a NP array), where the NP LSPs can simultaneously couple to SPP modes associated with charge-density waves on both surfaces, leading to a particularly rich dispersion behavior.

A schematic cross-sectional view of the investigated geometry is shown in Fig. 1(a), where both the metal (Ag) film and the overlaying dielectric (ZnS) layer have nanoscale thicknesses. In this geometry, the SPPs on the top and bottom surfaces of the Ag film are strongly coupled to each other, resulting in a large splitting of their dispersion curves and in the formation of even and odd hybrid modes. Examples of the intensity profiles of these SPP modes are plotted in Fig. 1(a), as calculated at a free-space wavelength of 500 nm using a transfer-matrix approach.⁷ The odd modes extend spatially across the entire structure including the Ag NP array, where they can further couple to the NP LSPs leading to an additional anticrossing in the plasmonic dispersion spectrum. At the same time, they also feature substantial (and geometrically tunable) penetration into the substrate, where a waveguide or optoelectronic active layer designed to operate at similar wavelengths may be located. The latter property provides an important advantage of the present geometry over coupled LSP-SPP systems involving a single metal-dielectric interface.

With this aim in mind, the substrate material used in the present work is GaN, which provides a convenient platform for the development of visible-range photonic devices (such as light emitters and solar cells) that may strongly benefit from plasmonic interactions.^{8–12} ZnS is utilized as the dielectric spacer layer because of its close refractive-index match to GaN (which enables a particularly strong coupling between the SPP modes supported by the two metal surfaces), in addition to ease of fabrication and low optical losses at visible wavelengths. The resulting plasmonic dispersion

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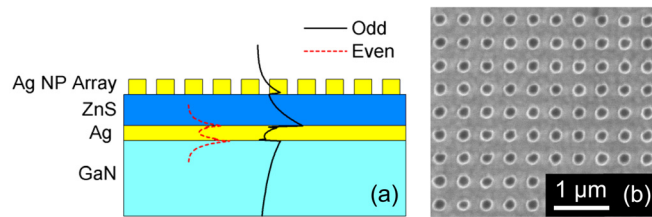


FIG. 1. (a) Schematic cross section of the sample geometry studied in this work, and field intensity profiles of the odd and even SPP modes at a free-space wavelength of 500 nm, calculated for the case of a 20-nm-thick Ag film and a 50-nm-thick ZnS layer. (b) SEM image of a Ag NP array fabricated on a Ag/ZnS film combination on a GaN substrate.

curves can be geometrically tuned by varying the Ag and ZnS film thicknesses, as well as the NP geometry. The structure of Fig. 1(a), therefore, provides an attractive ultra-compact system for the coupling of substrate-embedded optoelectronic/plasmonic devices to free space radiation with high angular tunability.¹³

II. EXPERIMENTAL AND SIMULATION METHODS

In order to study the plasmonic dispersion properties of these systems, several square-periodic NP arrays of different period Λ were fabricated on the same Ag/ZnS film combination deposited on a GaN substrate, and then tested via broadband transmission measurements at normal incidence. Each array can provide the additional in-plane wavevector $k_{array} = \frac{2\pi}{\Lambda} \sqrt{p^2 + q^2}$ to the incident light, where p and q are integers determining the diffraction order. As a result, incident photons of suitable energy (depending on Λ) can be diffractively coupled into even and odd SPP modes guided by the Ag film, leading to well defined minima in the sample transmission spectrum. At the same time, the incident light can also be directly attenuated by the NPs via absorption and scattering in the spectral vicinity of their LSP resonance. By plotting the energies of the measured transmission minima as a function of the array wavevector k_{array} , the full dispersion relation of the coupled NP-film system can then be reconstructed.

Three Ag film thicknesses (15, 20, and 25 nm) and three ZnS film thicknesses (50, 75, and 100 nm) were studied, resulting in a total of nine film combinations, in order to fully demonstrate the ability to engineer the plasmonic dispersion properties of these systems. To fabricate each sample, a 2.5-nm-thick Ni adhesion layer and the Ag thin film are first deposited on an RCA-cleaned GaN substrate using electron beam evaporation. The ZnS spacer layer is then formed over the Ag film using thermal evaporation, which is followed by fabrication of the NP arrays based on electron beam lithography and liftoff. In each array, the Ag NPs have cylindrical shape with 100-nm diameter and 30-nm height and include a 2.5-nm-thick bottom adhesion layer made of Ni. The array periods (ranging from 170 nm to 430 nm) and the NP dimensions were characterized using scanning electron microscopy (SEM); an exemplary SEM micrograph is shown in Fig. 1(b).

The optical transmission measurements were conducted for each NP-film geometry using broadband illumination at normal incidence with unpolarized light from a deuterium

tungsten halogen source. In these measurements, the samples are mounted on a piezo-controlled stage, allowing each array (whose overall dimensions are $50 \times 50 \mu\text{m}^2$) to be probed individually. Two long-working-distance 20 $\times$ objectives are used to focus the incident light on each array and to collect the transmitted signal, which is then analyzed with a fiber-coupled Ocean Optics USB-4000 grating spectrometer. Finally, the transmission spectra measured with the NP-film samples are normalized to the spectrum of the same Ag/ZnS film combination in the absence of the NP arrays, where no plasmonic modes can be excited.

Numerical simulations based on the finite-difference time-domain (FDTD) method were also conducted for each NP-film geometry investigated, using a commercial software package.¹⁴ In these calculations, the simulation region comprises a unit cell of the NP array (including the underlying ZnS and Ag films and the GaN substrate), with perfectly matched layers on the top and bottom boundaries and periodic boundary conditions in all other directions. The Ag, GaN, and ZnS layers are modeled with dielectric functions interpolated from tabulated experimental data.^{15–17} The structure is excited by a broadband total-field scattered-field source propagating in the direction perpendicular to the substrate surface (from the air side) and encompassing the entire NP grating and Ag film. This source allows the scattering and absorption contributions to the system response to be evaluated independently. The calculated absorption spectra are then utilized to determine the LSP resonance of the NP array and the absorption wavelengths associated with grating-coupled excitation of SPP modes propagating along the Ag film.

III. RESULTS AND DISCUSSION

Eight representative experimental-transmission and theoretical-absorption spectra are shown in Fig. 2 for NP-film structures with a 20-nm-thick Ag film and two different ZnS layer thicknesses [50 nm in Figs. 2(a) and 2(b), 75 nm in Figs. 2(c) and 2(d)]. The four spectra in each panel are offset relative to one another in the vertical direction for clarity and correspond (from the bottom to the top trace) to increasing values of the array period listed in the figure caption. Each experimental transmission spectrum has been low-pass filtered to minimize high-frequency components due to spectrometer noise or Fabry-Perot oscillations in the GaN substrate.

Three separate transmission minima can be identified in each experimental spectrum of Fig. 2(a), as indicated by the arrows. By comparing their spectral position versus array period with the calculated plasmonic dispersion curves (see Fig. 3), these minima are found to correspond, in order of increasing wavelength, to the excitation of a mode whose character is predominantly that of an odd SPP of the Ag film, that of the LSP resonance of the NP array, and that of an even SPP. Specifically, the relevant SPP modes here are those with wavevector $2\pi/\Lambda$, which can be excited by the normally incident light via first-order diffraction by the NP array. As the array period is increased, the SPP absorption features shift to longer wavelengths, determined by the

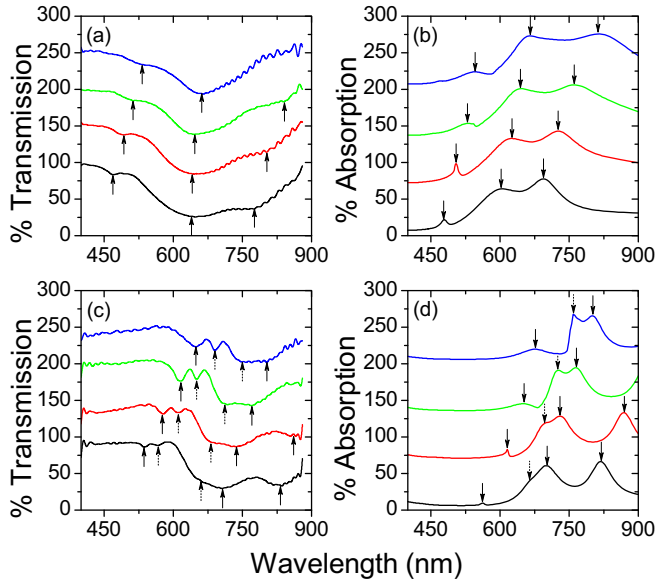


FIG. 2. Experimental transmission spectra [(a) and (c)] and calculated absorption spectra [(b) and (d)] of the geometry of Fig. 1(a) for different combinations of the relevant design parameters. In all panels, the Ag film thickness is 20 nm and the Ag NPs have 100-nm diameter and 30-nm height. In (a) and (b), the ZnS film thickness is 50 nm and the NP array period is 190, 210, 230, and 250 nm (from the bottom to the top trace). In (c) and (d), the ZnS film thickness is 75 nm and the NP array period is 250, 280, 310, and 340 nm (from the bottom to the top trace).

diffractive coupling condition and the multilayer dispersion relations. Interestingly, the transmission dip associated with the LSP resonance is also found to red-shift with increasing period, mostly due to the strong coupling between LSPs and SPPs in the systems under study. The spectra of Fig. 2(a) also reveal a large difference in linewidth between the even and odd SPP features, which is a direct consequence of their widely different absorption losses (with the odd modes generally having much longer propagation lengths¹ and correspondingly narrower transmission dips). The LSP features are relatively broad, which is partly attributed to the small interparticle spacings of the investigated arrays.¹⁸ The corresponding theoretical absorption spectra of Fig. 2(b) are in generally good agreement with the experimental data, with regards to the number and spectral properties of the features observed.

Similar considerations apply to the experimental spectra of Fig. 2(c), with the additional presence of two other transmission minima indicated by the dashed arrows. One of these new features (i.e., the broad dip close to the LSP resonance) also appears in the theoretical absorption spectra of Fig. 2(d), and is due to the excitation of the even SPP mode with wavevector $2\sqrt{2}\pi/\Lambda$ via second-order diffraction ($p=q=1$) of the incident light. The other, much narrower, additional dip is attributed to a grating-coupled odd SPP resonance for vertically polarized light (i.e., with the optical field perpendicular to the substrate surface).⁵ In our

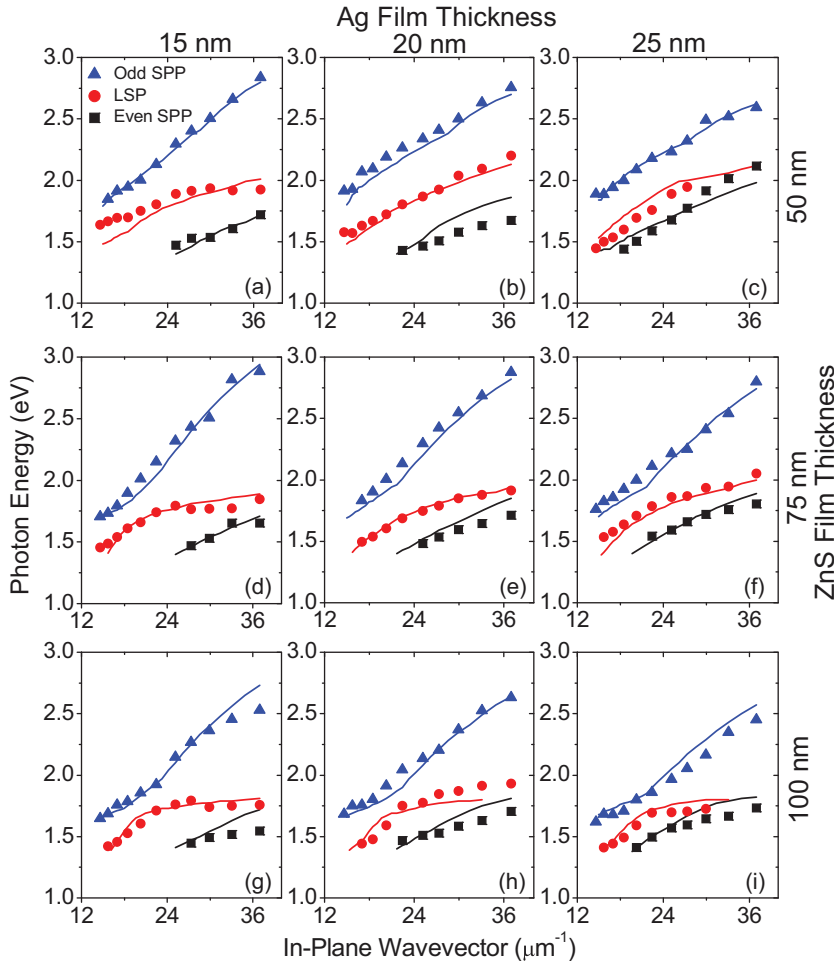


FIG. 3. Experimental (symbols) and theoretical (solid lines) plasmonic dispersion curves of the geometry of Fig. 1(a) for different combinations of the relevant design parameters. In all panels, the Ag NPs have 100-nm diameter and 30-nm height, and the NP array period Λ is related to the in-plane wavevector k according to the first-order diffraction condition $k = 2\pi/\Lambda$. The ZnS film thickness is 50 nm [panels (a), (b), (c)], 75 nm [(d), (e), (f)], and 100 nm [(g), (h), (i)]. The Ag film thickness is 15 nm [panels (a), (d), (g)], 20 nm [(b), (e), (h)], and 25 nm [(c), (f), (i)].

experiments, the incident light contains a small but non-negligible vertical polarization component as it is focused onto the sample by a high-numerical-aperture objective lens and, therefore, can excite such resonance. In contrast, in the FDTD simulations, the incident light is a plane wave at normal incidence, so that its vertical component is strictly zero and no such resonance is computed. The center wavelength of this new transmission dip is close to, but slightly shifted from, that of the main odd-SPP feature, which originates from diffraction of the horizontally polarized incident light and, therefore, can couple and anticross with the spectrally nearby horizontally polarized LSP resonance. Its narrow linewidth is again attributed to the long lifetime of the odd SPP modes. In Fig. 2(a), both additional features just described are likely masked by the nearby broad LSP transmission minima and, therefore, cannot be resolved.

In Fig. 3, we show the plasmonic dispersion curves of all the structures investigated in this work, corresponding to the aforementioned nine Ag/ZnS film thickness combinations. These traces were constructed by plotting the photon energies of the experimental transmission minima (symbols) and of the simulated absorption maxima (solid lines) as a function of $2\pi/\Lambda$. SPP modes excited via second- or higher-order diffraction, while present in some of the experimental and theoretical spectra, are omitted from these plots for simplicity. Three branches are obtained for each structure, which are labeled as even SPP, odd SPP, and LSP based on their asymptotic character in the limit of no NP-film coupling. In reality, such coupling can be quite strong in the structures under study, particularly in the vicinity of the anticrossing between the odd-SPP and LSP branches, and as a result many of the excited plasmonic modes have a hybrid LSP/SPP character. The overall agreement between the experimental and theoretical data shown in Fig. 3 is fairly good. Possible sources of discrepancy include experimental uncertainties in the NPs and films dimensions, surface roughness, and the use of bulk dielectric functions to model nanostructures in the FDTD simulations.

Two properties of the dispersion maps plotted in this figure are particularly significant and should be emphasized. First, a large energy separation between the even and odd SPP branches is observed, which decreases with increasing Ag film thickness t_{Ag} [e.g., see Figs. 3(d), 3(e), and 3(f) for $t_{Ag} = 15, 20$, and 25 nm]. This splitting indicates strong coupling between the SPP modes supported by the top and bottom surfaces of the Ag film, which in the limit of large t_{Ag} have nearly overlapping dispersion curves due to the similar refractive indexes of GaN and ZnS. Second, a clear anticrossing between the odd-SPP and LSP branches is also observed, caused by the strong spatial and spectral overlap between the underlying excitations. The size of this anticrossing gap can, therefore, be controlled by varying the thickness t_{ZnS} of the ZnS spacer between the Ag film and the NPs [e.g., it substantially decreases in going from Fig. 3(b) to 3(e) to 3(h) as t_{ZnS} is increased from 50 to 75 to 100 nm]. At the smallest measured t_{ZnS} of 50 nm, the LSP/odd-SPP coupling is so strong that the resulting anticrossed dispersion curves appear as nearly parallel to each other. In contrast, no indications of anticrossing between the even-SPP and LSP

branches are observed, even as these two branches approach each other in the limit of large wavevectors. The reason is that in this limit all SPP modes are increasingly localized to the supporting Ag film, and therefore, their spatial overlap with the overlaying NP array becomes negligibly small.

IV. CONCLUSIONS

In summary, we have presented a detailed experimental and theoretical study of the plasmonic properties of ultrathin Ag films embedded in a symmetric dielectric environment and strongly coupled to nearby Ag NP arrays. Specifically, the plasmonic dispersion curves of these systems have been measured for various combinations of their key geometrical parameters, and numerical simulations have been carried out to help identify their physical nature. Propagating SPPs associated with both even and odd charge oscillations on the two surfaces of the metal film have been observed, with the latter modes featuring relatively narrow linewidths indicative of reduced propagation losses. Furthermore, a strong mixing between these odd SPPs and the LSP resonances of the nearby NP array has been obtained, as evidenced by the large anticrossing of their respective dispersion curves. These results clearly indicate that coupled metal NP-film systems can be developed that support widely tunable, hybrid LSP/SPP excitations with strong coupling to free-space radiation and at the same time substantial penetration depth into the substrate. These properties are attractive for the development of plasmon-enhanced optoelectronic devices that can be diffractively-coupled to free space in a highly controllable fashion.

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